Application of Geminal Methods to Molecular Calculations

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The energy of a molecule is expressed as a summation involving the expectations values of a two-electron Hamiltonian. An approximation which has been used for atomic systems, involving the weight factors in this summation, was made to evaluate the energies for the lithium molecule and of an isolated lithium atom. It was found that at 4.0 a. u. the bonding energy was of the correct order of magnitude, but the correlation energy of the system was overestimated giving an error in the total energy of the molecule of 1.3%. An alternative approximation for the evaluation of the summation was proposed, and it was found to give rise to an error of 0.3% in the total energy and a bonding energy of the correct order of magnitude. Attention is given to the application of geminal methods to larger systems.

I. INTRODUCTION

As every chemist knows, the energy of a covalent crystal such as diamond can be estimated quite accurately by adding together the energies of the separated carbon atoms and the bond energies of adjacent atoms. Because only interactions between adjacent atoms are large, the energy is clearly an extensive thermodynamic property. Within the framework of *ab initio* quantum chemistry, it is much more difficult to demonstrate this extensive property.

If the Hamiltonian of the system can be adequately approximated by a sum of one-electron operators using effective potentials, the energy may be expressed as the expectation value of a reduced one-particle Hamiltonian with the charge density. The charge density, to a good approximation, may be expressed as a sum of contributions from independent groups of electrons. Hence in the independent particle model with localized orbitals the chemical picture is recovered.

The energy of a system can always be written exactly as the expectation value of a two-particle reduced Hamiltonian with the second-order reduced density matrix. For N electrons, the two-particle density contains at least $N(N-1)/2$ important terms. Hence the two-particle density is not obtainable by simply summing contributions from localized groups. This paper discusses some difficulties in approximating this density matrix for a diatomic system. Some suggestions are made which could lead to improved approximations for larger systems.

II. THE MOLECULAR GEMINAL WAVE FUNCTION

A trial function for an N-electron molecule may be written as

$$\Psi(12\cdots N) = \sum_{n_1\cdots n_{N/2}} a_{n_1\cdots n_{N/2}} \Phi_{n_1}(12)$$
$$\times \Phi_{n_2}(34)\cdots\Phi_{n_{N/2}}(N-1,N) \tag{1}$$

for even N, or

$$\Psi(12\cdots N) = \sum_{n_1\cdots n_{(N+1)/2}}$$
$$\times a_{n_1}\cdots a_{(N+1)/2}\Phi_{n_1}(12)\cdots$$
$$\times \Phi_{n_{(N-1)/2}}(N-2,N-1)d_{(N+1)/2}(N) \tag{2}$$

for N odd, where the $a_n\cdots a_m$ are restricted in such a manner that the total wave function is antisymmetric and $\{\phi_n d_n\}$ is an orthonormal set of functions. The second-order reduced density matrix of this wave function is

$$D(12,1'2') = \sum_{nm} B_{nm}\Phi_n(12)\Phi_m(1'2'), \tag{3}$$

where the weight factors

$$B_{nm} = \sum_{n_2\cdots n_M} a_{nn_2\cdots n_M} a^*_{mn_2\cdots n_M} \tag{4}$$

are normalized so that

$$\sum_n B_{nn} = 1. \tag{5}$$

The energy expectation value with respect to the Hamiltonian

$$\mathcal{K}(12\cdots N) = g_0 + \sum_{i=1}^{N} g_1(i) + \sum_{i>j}^{N} g_2(ij) \tag{6}$$

is

$$E = \tfrac{1}{2}N\sum B_{nm}\epsilon_{nm}, \tag{7}$$

where

$$\epsilon_{nm} = \langle \Phi_n \bar{h}\Phi_m\rangle, \tag{8}$$

$\bar{h}(12)$ being the reduced Hamiltonian to $\mathcal{K}(12\cdots N)$,

$$\bar{h}(12) = 2g_0/N + g_1(1) + g_1(2) + (N-1)g_2(12). \tag{9}$$

This expression may be minimized with respect to the B_{nm}, subject to the restrictions inherent in the $a_{n_1\cdots nN/2}$.[1] It is hoped that, with an appropriate choice of the geminal basis set, such an energy sum will

converge rapidly to a limit which is close to the true energy, indicating that the geminal-sum wave function is a useful trial function even when a truncated basis set of geminals is used. In the case of atoms, a choice of geminals which diagonalize the reduced Hamiltonian is found to be appropriate since they account for electron correlation and give rise to a summation in Eq. (7) having no off-diagonal terms. This method yields fairly good energies using a particularly simple approximation for the B_{nn}; the "zero-order approximation," [2,3] which is related to a method of Bopp.[4] In such an approximation the $B_{nn}{}^{(0)}$ are given the values they would have if they were derived from a single determinantal wave function. A correspondence is made between the Φ_n and a linear combination of the 2×2 two determinants obtained on expanding the $N \times N$ determinant. Generally certain doubly excited metastable energy levels of $\bar{h}$ are included.

Investigation of such a function (1) in the case of molecules, may thus be made using this zero-order approximation for the B_{nn}, which does not involve the total satisfaction of the antisymmetrization condition and hence may give energies which lie below the "true" energy. The treatment could be extended by calculating the B_{nn} through a variational calculation with the satisfaction of the antisymmetrization condition[1,5,6] or by using the zero-order approximation for the B_{nn} as the zero-order trial function in a perturbation series.

In the case of the neutral homonuclear diatomic molecules having a nuclear charge of Z and N ($N = 2Z$) electrons, it is convenient to scale the lengths and energy of the reduced Hamiltonian by the nuclear charge giving rise to the scaled-reduced Hamiltonian,

$$\bar{h}(r_1, r_2, R) = Z^2 \bar{h}'(Zr_1, Zr_2, ZR) \quad (10)$$

in atomic units, that is,

$$\bar{h}'(12) = -\tfrac{1}{2} \nabla_2'^2 - \tfrac{1}{2} \nabla_2'^2 - \frac{1}{r_{A_1}'}$$
$$- \frac{1}{r_{A_2}'} - \frac{1}{r_{B_1}'} - \frac{1}{r_{B_2}'} + \frac{\gamma}{r_{12}'} + \frac{1}{R'}, \quad (11)$$

where $\gamma = (2Z - 1)/Z$; thus $1 < \gamma < 2$.

The potential energy curves of the diatomic molecules may be expressed in terms of summations involving pair energies E_n' which are eigenvalues to the Hamiltonian (11). These pair energies will change through the molecular series as a function of the interelectronic interaction parameter γ.

Certain of the pair energies will be bonding and others nonbonding. If the $B_{nn}{}^{(0)}$ are the dominant terms in the energy sum then it should be possible to employ concepts of "bond" and "bond order" using the pair energies and their weight factors.

III. CALCULATION

A calculation has been made for the He_2 system using rather simple geminals,[7] and the error was found to be of the order of 1% and constant for a large range of internuclear separation. In the present paper, the Li_2 system is considered in which correlation is more important and for which the minimum in the potential energy curve is very shallow.

A method of calculating potential energy curves for diatomic molecules has been developed[8,9] using a combination of self-consistent-field (SCF) configuration interaction and perturbation theory.[10]

It was decided to calculate the potential energy curves for the energy levels to the reduced Hamiltonian of the Li_2 molecule using this method. It should be noted, however, that in the case of a Hamiltonian having an interaction term as large as $5e^2/r_{12}$, the use of perturbation theory to calculate corrections to a SCF energy is not strictly justified. The calculations were performed at a single internuclear separation of 4.0 a.u. and the results are given in Table I.

The energies of the reduced Hamiltonian to the Li atom, calculated by the same method, are shown in Table II. Using the zero-order approximation the energy of the Li_2 molecule is -15.2516 a.u. while twice that of the Li atom is -15.1750 a.u. indicating that, in this approximation, the molecule is stable with a binding energy of 0.077 a.u. The binding energy is of the correct order of magnitude when compared with the experimental result of 0.03 a.u.; however, the total energy of the system is in error by 1.3%, since the "experimental nonrelativistic"[11] energy of two lithium atoms is -14.9561 a.u.

In these calculations the SCF energy was first solved for the desired configuration. Since some of these configurations corresponded to metastable states, this proved difficult (notice, for instance, that $1\sigma_u 2\sigma_g$ is lower in energy than $1\sigma_u 1\sigma_g$ because of the large electron repulsion). The correlation energies were estimated by second-order perturbation theory using all configurations except the other occupied geminals. The correlation energy contributions from the other occupied geminals were omitted because they tended to cancel in E. For instance, the energy lowering of $1\sigma_g^2$ by $1\sigma_u^2$ in second order is the same as the energy increase of $1\sigma_u^2$ by $1\sigma_g^2$. Without this constraint this pair of nearly-degenerate eigengeminals changes to $1\sigma_g^2 \pm 1\sigma_u^2$ with energies -8.4860 and -1.700 a.u. $1\sigma_g^2 - 1\sigma_u^2$ is nearly $1s_a 1s_b$ with zero correlation energy and $1\sigma_g^2 + 1\sigma_u^2$ is an ionic geminal with large (0.88 a.u.) correlation energy. In reading Table I, it should always be kept in mind that any bound-state eigenvalue of $\bar{h}$ must lie at least as low as -4.5 a.u. which is the energy for one electron in the $1\sigma_g$ orbital and the other in an unbound orbital of zero kinetic energy.

IV. OVERESTIMATION OF THE ENERGY

As was the case with atoms, the use of the zero-order approximation overestimates the energy of the Li_2 system. A simple argument indicates that this is likely to be the case for other members of the series of homonuclear diatomic molecules.

In the following argument the wave functions used are not eigenfunctions of spin but an exten-

TABLE I. The calculated energies of the reduced Hamiltonian of the lithium molecule. [a]

Configuration		SCF energy (a.u.)	Correlation energy (a.u.)	B_{nn}^{0}
$1\sigma_g^{2}$	$^{1}\Sigma_g^{+}$	−5.0973	0.2078	$\frac{1}{15}$
$1\sigma_u^{2}$	$^{1}\Sigma_g^{+}$	−5.0584	0.2040	$\frac{1}{15}$
$1\sigma_g1\sigma_u$	$^{1}\Sigma_u^{+}$	−2.3635	0.2567	$\frac{1}{15}$
$1\sigma_g1\sigma_u$	$^{1}\Sigma_u^{+}$	−8.4859	0.0000	$\frac{1}{5}$
$1\sigma_g2\sigma_g$	$^{1}\Sigma_g^{+}$	−4.5887	0.1731	$\frac{1}{15}$
$1\sigma_g2\sigma_g$	$^{1}\Sigma_g^{+}$	−4.6421	0.1075	$\frac{1}{5}$
$2\sigma_g^{2}$	$^{1}\Sigma_g^{+}$	−0.9044	0.0743	$\frac{1}{15}$
$1\sigma_u2\sigma_g$	$^{1}\Sigma_u^{+}$	−4.2628	0.1841	$\frac{1}{15}$
$1\sigma_u2\sigma_g$	$^{1}\Sigma_u^{+}$	−4.3390	0.0536	$\frac{1}{5}$

[a] $h = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 3\left(\frac{1}{r_{a_1}} + \frac{1}{r_{b_1}} + \frac{1}{r_{a_2}} + \frac{1}{r_{b_2}}\right) + 5/r_{12} + 3/R,$

$E = 3\sum B_{nn}^{0}\epsilon_n.$

TABLE II. The calculated energies of the reduced Hamiltonian of the lithium atom. [a]

Configuration	SCF energy (a.u.)	Correlation energy	B_{nn}^{0}
$1s^2$ ^{1}S	−5.6439	0.1411	$\frac{1}{3}$
$1s2s$ ^{3}S	−4.6492	0.0046	$\frac{1}{2}$
$1s2s$ ^{1}S	−4.7077	0.0010	$\frac{1}{6}$

[a] $h = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 3\left(\frac{1}{r_{a_1}} + \frac{1}{r_{a_2}}\right) + \frac{2}{r_{12}},$

$E = \frac{3}{2}\sum B_{nn}^{0}\epsilon_n.$

sion (in which linear combination of Slater determinants are taken), which preserves the essential features. A good wave function for a molecule is

$$\Psi = \sum_{lk} C_{lk}\left(Q_1\overline{Q}_1 \cdots Q_N\overline{Q}_N, \frac{Q_l\overline{Q}_l}{Q_k\overline{Q}_k}\right)$$

$$+ C^0(Q_1\overline{Q}_1 \cdots Q_N\overline{Q}_N), \quad (12)$$

where l is not included in the set $1, 2 \cdots N$.

The energy corresponding to this function may be approximated by

$$E \approx E_{SCF} - \sum_{l,k} V_{lk}^2/\Delta E_{lk}, \quad (13)$$

$$E \approx E_{SCF} - \sum_{l,k} \Delta_{l,k}, \quad (14)$$

where E_{SCF} is the energy calculated using the single determinant, ΔE_{lk} is the difference be-

tween the energy expectation values of the pair $Q_l\overline{Q}_l$ and $Q_k\overline{Q}_k$, and V_{lk} is the matrix element of the interaction between these pairs.

The eigenfunctions to the reduced Hamiltonian may be written in terms of the same basis set as

$$\Phi_n(12) = \sum_i a_{ii} \Phi_i(1)\Phi_i(2), \quad (15)$$

where $_n a_{ii}$ is generally large for some value of i ($_n a_{11}$, say) and small for all others. Hence in second order the energy may be written

$$\epsilon_n = \epsilon_{11}^{n} - \sum_k [(N-1)V_{k1}]^2/\Delta E_{k1}, \quad (16)$$

that is

$$\epsilon_n = \epsilon_n^{SCF} - (N-1)^2\sum_l \Delta_{ln}'. \quad (17)$$

Hence in the zero-order approximation the total energy of the system is

$$E = \frac{1}{2}N\sum B_{nn}^{(0)}\epsilon_n^{SCF}$$

$$- (N-1)^2\frac{1}{2}N\sum B_{nn}^{(0)}\sum_l \Delta_{ln}'. \quad (18)$$

But $B_{nn}^{(0)} = 2/N(N-1)$, if each spin component is counted as a distinct state, so

$$E = (N-1)^{-1}\sum_n \epsilon_n^{SCF} - (N-1)\sum_{k,l}\Delta_{ln}'. \quad (19)$$

Now $(N-1)^{-1}\sum_n \epsilon_n^{SCF} < E_{SCF}$, since each ϵ_n^{SCF} lies below the expectation value of $\overline{h}$ (12) with respect to the corresponding SCF orbitals of $\mathcal{K}$ (12$\cdots N$). The V_{lk} and V_{lk}' are exchange integrals and are therefore nearly equal, and the E_{kl} depend mostly on differences in kinetic energy and hence are also about the same size. The overall effect is that the zero-order approximation tends to overestimate the correlation energy by a factor of $(N-1)$.

Such an argument suggests that the approximation

$$E = \frac{1}{2}N\sum B_{nn}^{(0)}\epsilon_n^{SCF}$$

$$- [N/2(N-1)]\sum B_{nn}^{(0)}\epsilon_n^{correlation} \quad (20)$$

may be much better than the zero-order approximation for calculating energies.

In the case of the Li_2 system, application of this approximation gives a value of -14.910 a. u. for the separated atoms and -14.998 a. u. for the molecule at 4.0 a.u., yielding a binding energy of -0.087 a. u. with respect to the calculated energy of the separated atoms or -0.042 a.u. with respect to the experimental energy of the separated atoms.

These total energies of the system lie within 0.3% of the experimental values while the binding energy is of the correct order of magnitude, and they indicate that such an approximation may be a powerful tool for the calculation of molecular potential energy curves.

V. WAVE-FUNCTION GROUPS

As one proceeds to calculate larger systems, the factor $N-1$ in the interelectronic interaction term of the reduced Hamiltonian increases. Indeed in the limit of a metal or long-chain polymer it approaches infinity. Clearly although the summation (7), involving the eigenvalues to this Hamiltonian, is still valid, it does not seem to involve a particularly useful approach to the problem.

In order to find a better approach, let us consider the wave function for a dilute gas of K identical neutral atoms with nuclear charge $Z=N$. The wave function to a good approximation is just

$$\psi(r_1 \cdots r_{KN}) = cA(1 \cdots KN)$$
$$\times \Pi_I \Phi_I(r_{1+(I-1)N}, r_{2+(I-1)N}, \cdots r_{IN}), \quad (21)$$

where $A = [(KN)!]^{-1/2} \sum_P (-1)^P P$,   (22)

$$c = (N!)^{-K/2}, \quad (23)$$

and the Φ_I are the wave functions for the individual atoms. If $D_I^{(2)}(1,2;1'2')$ and $D_I^{(1)}(1,1')$ are the reduced two- and one-particle matrices corresponding to the atomic wave functions Φ_I, then it is easy to show that the density matrices for the gas are

$$D^{(1)}(1,1') = \frac{1}{K} \sum_{I=1}^{K} D_I^{(1)}(1,1') \quad (24)$$

and

$$D^{(2)}(1,2;1'2') = \frac{(N-1)}{K(NK-1)} \sum_{I=1}^{K} D_I^{(2)}(12;1'2')$$
$$+ \frac{N}{K(NK-1)} \sum_{I>J} (1 - P_{1'2'})$$
$$\times (1 - P_{12})D_I^{(1)}(1,1')D_J^{(1)}(2,2'), \quad (25)$$

where P_{ij} is an operator permuting the electronic coordinates. This derivation holds only for isolated systems for which the Φ_I are nonoverlapping and are identical to the free-atom functions.

The Hamiltonian for the gas is

$$\mathcal{K} = \sum_{I<J} \frac{N^2}{r_{IJ}} + \sum_{i=1}^{KN} \left[-\frac{1}{2}\nabla_i^2 - N\sum_{I=1}^{K} \frac{1}{r_{iI}} \right] + \sum_{i<j}^{KN} \frac{1}{r_{ij}} \quad (26)$$

which has the following reduced Hamiltonian

$$h = \frac{2N}{K} \sum_{I<J} \frac{1}{r_{IJ}}$$
$$+ \sum_{i=1}^{2} \left[-\frac{1}{2}\nabla_i^2 - N\sum_{I=1}^{K} \frac{1}{r_{iI}} \right] + \frac{(KN-1)}{r_{ij}}. \quad (27)$$

Consequently the energy of the gas is

$$E = \frac{1}{2}KN \, \text{Tr}hD^{(2)}. \quad (28)$$

Let $D_\alpha^{(2)} = K^{-1} \sum_I D_I^{(2)}(1,2;1'2')$ (29)

and

$$D_\beta^{(2)} = \frac{1}{K(K-1)} \sum_{I>J} (1 - P_{1'2'})$$
$$\times (1 - P_{12})D_I^{(1)}(1,1')D_J^{(1)}(2,2') \quad (30)$$

so

$$D^{(2)} = \frac{N-1}{NK-1} D_\alpha^{(2)} + \frac{N(K-1)}{(NK-1)} D_\beta^{(2)}, \quad (31)$$

where $\text{Tr}D_\alpha^{(2)} = 1$, $\text{Tr}D_\beta^{(2)} = 1$.   (32)

Then

$$\frac{KN}{2} \text{Tr}hD_\alpha^{(2)} = \sum_{I<J} \frac{N^2}{r_{IJ}} + N\left[\sum_I g_{i,I} \right.$$
$$\left. - 2N\sum_{I<J} \frac{1}{r_{IJ}} \right] + \frac{1}{2}N(KN-1)\sum_I g_{2,I} \quad (33)$$

$$\frac{KN}{2} \text{Tr}hD_\beta^{(2)} = \sum_{I<J} \frac{N^2}{r_{IJ}} + N\left[\sum_I g_{1,I} \right.$$
$$\left. - 2N\sum_{I<J} \frac{1}{r_{IJ}} \right] + \frac{[N(KN-1)]}{(K-1)} \sum_{I<J} \frac{1}{r_{IJ}}, \quad (34)$$

where $g_{1,I} = \text{Tr}\left[-\frac{1}{2}\nabla_1^2 - N/r_{1I} \right]D_I^{(1)}$,   (35)

$$g_{2,I} = \text{Tr}[r_{12}^{-1}D_I^{(2)}]. \quad (36)$$

Since $E_I = Ng_{1,I} + \frac{1}{2}N(N-1)g_{2,I}$,   (37)

$$\frac{KN}{2} \text{Tr}D_\alpha^{(2)} = \sum_I E_I$$
$$+ \frac{N(K-1)}{2} \sum_I g_{2,I} - \sum_{I<J} \frac{N^2}{r_{IJ}}, \quad (38)$$

$$\frac{KN}{2} \text{Tr}hD_\beta^{(2)} = \sum_I Ng_{1,I} + \frac{N(N-1)}{K-1} \sum_{I<J} \frac{1}{r_{IJ}}. \quad (39)$$

Finally, (28) reduces to

$$E = \sum_I E_I. \quad (40)$$

It is interesting to note that, in the limit of large K, $D_\beta^{(2)}$ becomes the dominant part of $D^{(2)}$ in the sense that $D_\beta^{(2)}$ gives the entire normalization integral and the entire contribution to $D^{(1)}$. In fact, as $K \to \infty$

$$\frac{KN}{2} \text{Tr}h\left[\frac{N-1}{KN-1} D_\alpha^{(2)} \right] \to \sum_I \frac{N(N-1)}{2} g_{2,I} \quad (41)$$

and $\frac{KN}{2} \text{Tr}h\left[\frac{N(K-1)}{(KN-1)} D_\beta^{(2)} \right] \to \sum_I Ng_{1,I}$ (42)

Hence even though $D_\alpha^{(2)}$ gives no contribution to $D^{(1)}$, it gives the entire electron repulsion of the separate atoms and must be accurately approximated.

In order to see how $D^{(2)}$ might be approximated for interacting systems, let us consider a simple case in which each Φ_I is approximated by a single Slater determinant with orbitals ϕ_{iI}. Then

$$D_I^{(2)} = \frac{2}{N(N-1)} \sum_{i<j} \frac{1}{\sqrt{2}} |\phi_{iI}^{(1)} \phi_{jI}^{(2)}|$$
$$\times \frac{1}{\sqrt{2}} |\phi_{iI}^{*}(1') \phi_{jI}^{*}(2')| \quad (43)$$

or $$D_I^{(2)} = \frac{2}{N(N-1)} \sum_{i<j} D_{ijII}^{(2)} \quad (44)$$

where $D_{ijII}^{(2)}$ is the density matrix for the two-electron wave function $\psi_{ijII} = (1/\sqrt{2}) |\phi_{iI}^{(1)} \phi_{jI}^{(2)}|$. Similarly

$$\tfrac{1}{2}(1 - P_{1'2'})(1 - P_{12})D_I(1,1')D_J(2,2')$$

$$= \sum_{i<j} D_{ijIJ}^{(2)}, \quad (45)$$

where $D_{ijIJ}^{(2)}$ is the density matrix for

$$\psi_{ijIJ} = (1/\sqrt{2}) |\phi_{iI}(1) \phi_{jJ}(2)| \quad . \quad (46)$$

Hence $$D^{(2)} = \frac{2}{KN(KN-1)} \sum_{(iI)<(jJ)} D_{ijIJ}^{(2)}, \quad (47)$$

where $(iI) = i + (N-1)I$, and

$$\bar{E} = \frac{1}{(KN-1)} \sum_{(iI)<(jJ)} \text{Tr}(hD_{ijIJ}^{(2)}). \quad (48)$$

In order to obtain a better approximation to the total energy, it might be possible to retain this expression for $D^{(2)}$ and $\bar{E}$ with $D_{ijIJ}^{(2)}$ generated from a different ψ_{ijIJ}. It would be desirable if this could be done by solving an eigenvalue equation of the form

$$h_{ijIJ} \psi_{ijIJ} = \epsilon_{ijIJ} \psi_{ijIJ}, \quad (49)$$

so that some interactions between atoms could be included. One reasonable way of doing this would be to write

$$h_{ijIJ} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + v_{ijIJ} + r_{12}^{-1}, \quad (50)$$

where

$$v_{ijIJ} = \sum_{k=1}^{2} \sum_{L=1}^{K} \left[-\frac{N}{r_{kL}} + \sum_p' \int \frac{d\tau_q |\phi_{p,L}(q)|^2}{r_{qk}} \right] \quad (51)$$

and the $\sum'$ indicates that the terms containing ϕ_{iI} or ϕ_{jJ} are omitted. This is equivalent to solving the two-electron problem in the effective field of $K-2$ neutral atoms and two positive ions I^+ and J^+ (neglecting exchange potentials). The ϕ_{iI} represent the Hartree-Fock orbitals of the unperturbed atoms. For $I = J$, this reduces to solving for a two-

electron wave function in the field of I^{++} and $K-1$ neutral atoms.

This procedure is not completely impractical when applied to a crystal. The integrals involved in calculating ψ_{ijIJ} by a variational procedure would give without any additional effort $\text{Tr}(r_{12}^{-1}D_{ijIJ}^{(2)})$, $\text{Tr}[(r_{1I}^{-1} + r_{2I}^{-1})D_{ijIJ}^{(2)}]$, and $\text{Tr}[(\nabla_1^2 + \nabla_2^2)D_{ijIJ}^{(2)}]$. Hence $\text{Tr}(hD^{(2)})$ could be evaluated without the use of additional integrals. The equations are also reasonable in the sense that, if the effective potential of a neutral atom is neglected and the ψ_{ijIJ} are solved in the open shell SCF approximation, the sum of the atomic SCF energies would be recovered in the case of a dilute gas. If the SCF approximation is not used, then the eigenvalues of h_{ijII} would lie below the SCF result by about the pair-correlation energy of the ij pair. The eigenvalues of h_{ijIJ} $(I \neq J)$ for a dilute gas would be given exactly by the open-shell SCF solution.

For a two-electron atomic problem, the decrease in $\langle r_{12}^{-1} \rangle$ for a correlated wave function is about twice the correlation energy, and the increase in $\langle -\tfrac{1}{2}\nabla^2 \rangle$ is about equal to the correlation energy. Since the average electron repulsion for an atom comes entirely from the $D_{ijII}^{(2)}$, whereas the kinetic energy comes primarily from the $D_{ijIJ}^{(2)}$ (for which it is unshifted by correlation), the value of E in this approximation would be below the real total energy of all the atoms by their total correlation energy.

It is interesting to compare these approaches for a homonuclear diatomic molecule in the limit of infinite internuclear separation for the simple example of the four-electron molecule A_2.

The energy of the molecule A_2 having nuclear charge Z is given by the summation (7) as

$$E = 2 \sum B_{nm} \epsilon_{nm} \quad . \quad (52)$$

The single determinantal wave function for A_2 consists of a 4×4 determinant of $1S$ orbitals on atoms A. Hence in the zero-order approximation at the limit of infinite internuclear separation

$$E = 2[\tfrac{2}{3}E_1 + \tfrac{1}{3}E_2] \quad , \quad (53)$$

where E_1 is twice the energy of the ground state of an electron associated with a nuclear charge A, and E_2 is the ground-state energy of a two-electron atom having nuclear charge Z and an interelectronic interaction term $(2Z-1)^2/r_{12}$.

The energy given by (53) should be just twice the energy $E(Z)$ of the two-electron atom having charge Z. Hence

$$2E(Z) \simeq \tfrac{1}{3}[8Z^2 E_H + 2E_2] \quad , \quad (54)$$

where E_H is the energy of a hydrogen atom. If the reduced Hamiltonian is scaled by a factor of $(N-1)$, the above expression becomes

$$E(Z) \simeq \tfrac{1}{6}[8Z^2 E_H + 18E(Z/3)] \quad . \quad (55)$$

Hence a comparison of the two methods yields a relationship between the energy of two-electron

atom having charges Z and $Z/3$. From a perturbation expansion, in Z^{-1}, for atomic energies

$$E(Z) = Z^2\epsilon_0 + Z\epsilon_1 + \epsilon_2 + \cdots \ . \tag{56}$$

and

$$E(Z/3) = (Z/3)^2\epsilon_0 + Z/3\epsilon_1 + \epsilon_2 + \cdots \ . \tag{57}$$

Therefore the following relationship is found:

$$E(Z) = 3E(Z/3) + \tfrac{4}{3}Z^2 E_H - 2\epsilon_2 + 0(\epsilon_3); \tag{58}$$

that is, the two methods agree except for second-order terms or correlation terms in the energy.

VI. CONCLUSION

The zero-order approximation is found to have the same degree of success in this molecular example as in the case of atomic calculations. That is, the energy lies below the true energy by the order of 1% owing to the overestimation of the correlation energy. The energy difference between the

two internuclear separations of a molecule is of the correct order of magnitude, similarly the energy difference between two excited states of an atom is given to within 0.3% in the atomic case.[3] The argument which indicates why the correlation energy is overestimated also yields an improved approximation. It appears that by using the minimum number of geminals and screening the energies in the correct manner, a good result is obtained for the energy of a molecular system. An extension of such methods to larger systems is possible if the geminals are carefully selected. It is desirable that rapid convergence of the energy summation is achieved, and to this end the two-electron eigenfunctions of an effective field problem may be used as the basis for the wave function of such a system.

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[1]F. D. Peat and R. J. C. Brown, Intern. J. Quantum Chem. **S1**, 465 (1967).

[2]T. B. Grimley and F. D. Peat, Proc. Phys. Soc. (London) **86**, 249 (1965).

[3]F. D. Peat and R. J. C. Brown, Can. J. Phys. **44**, 1344 (1966).

[4]F. Boop, Z. Physik **156**, 348 (1959).

[5]F. D. Peat, "Reduced Density Matrices with Applications to Physical and Chemical Systems"–Survey lectures and contributed papers of a Conference held at Queen's University, Kingston, Ontario, 1967, edited by

A. J. Coleman and R. M. Erdhal. Queen's Papers in Pure and Applied Mathematics, No. 11.

[6]F. D. Peat, to be published.

[7]F. D. Peat, Can. J. Chem. **45**, 847 (1967).

[8]C. F. Bender and E. R. Davidson, J. Chem. Phys. **47**, 4472 (1967).

[9]C. F. Bender and E. R. Davidson, J. Phys. Chem. **70**, 2675 (1966).

[10]E. R. Davidson, J. Chem. Phys. **48**, 3169 (1968).

[11]C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).